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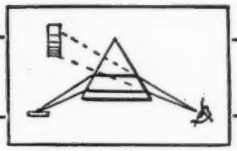

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Chromaticity Limitations of the Best Physically Realizable Three-Filter Photoelectric Colorimeter

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(Received November 1, 1937)

The theoretical requirements to be met by a photoelectric colorimeter capable of yielding I.C.I. tristimulus values, and relationships between tristimulus values and instrumental reflectances are given. For practical reasons, the correct photoelectric colorimeter must be equipped with four filters. It is commonly believed that a three-filter photoelectric colorimeter would be generally suitable for color specification and color matching; this is tested from the theoretical standpoint, and it is shown that the best physically realizable three-filter photoelectric colorimeter would suffer a fundamental chromaticity limitation. Relationships between the displacements of instrumental points on the chromaticity diagram and errors in the "red," green, and blue reflectances are given. Especial attention is given to errors originating in the assumption that the blue reflectance may be used in the evaluation of both the X and Z tristimulus values; maximal displacements associated with this assumption are given for a number of points on the diagram, and it is shown that actual chromaticity errors would be objectionably great for many colors of importance. The use of a three-filter photoelectric colorimeter as a color comparator is discussed.

I. INTRODUCTION

DURING the past few years a number of instrument manufacturers in this country and abroad have produced photoelectric "color analyzers," "color comparators," "colorimeters," "reflection meters," etc., for which broad claims have been made.[1] In addition to these commercially available instruments there is an indeterminable number of "home-made" devices constructed by technical men in industry who are earnestly attempting to make the routine control of color less subjective. Recently, as part of an instrumentation program sponsored by the American Paper and Pulp Association, the writer and his co-workers[2] have investigated several photoelectric instruments of the non-spectrophotometric or multi-filter type. During the course of this work it has become increasingly apparent that many of the designers of existing instruments have paid little or no attention to basic colorimetric requirements; large errors of geometrical, spectral, and photometrical origin have frequently been encountered.[3] It is the

[1] Discussions of photoelectric colorimeters and further literature references are given by K. S. Gibson, N.B.S. Letter Circular LC-473, and J. Guild, J. Sci. Inst. **11**, 76 (1934).

[2] Drs. P. Nolan and G. R. Sears of the physics staff, to whom the writer is indebted for helpful discussions on the subject of the present paper.

[3] The instrument manufacturer often places great stress on precision of reproducibility and stability rather than on fundamental accuracy. The distinction between precision and accuracy made by Gibson, J.O.S.A. **21**, 564 (1931), is particularly useful in a discussion of photoelectric colorimeters.

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purpose of this paper to establish the chromaticity limitations of the three-filter photoelectric colorimeter, and to present a means for estimating the errors in trichromatic coefficients obtained by such an instrument.

II. Theoretical Requirements

By the method of indirect colorimetry, the tristimulus values of the light reflected from a sample are

$$X=\int_0^\infty ER\bar{x}\,d\lambda, \quad Y=\int_0^\infty ER\bar{y}\,d\lambda, \quad Z=\int_0^\infty ER\bar{z}\,d\lambda, \tag{1}$$

where E is the relative spectral energy distribution of the illuminant, R is the spectral reflectance of the sample, and $\bar{x}$, $\bar{y}$, and $\bar{z}$ are the I.C.I. tristimulus functions for spectrum colors; E is here normalized to make Y the visual efficiency of the sample. It is generally appreciated that these integrals could hypothetically be evaluated by means of a photoelectric instrument equipped with filters, provided that the quantities k_x, k_y, and k_z in the equations

$$X=k_x\int_0^\infty E'RT_rS\,d\lambda, \quad Y=k_y\int_0^\infty E'RT_gS\,d\lambda, \quad Z=k_z\int_0^\infty E'RT_bS\,d\lambda \tag{2}$$

have the values,

$$k_x=E\bar{x}/E'T_rS, \quad k_y=E\bar{y}/E'T_gS,$$

and

$$k_z=E\bar{z}/E'T_bS,$$

and are each constant for all wave-lengths; in Eqs. (2), E' is the relative spectral energy distribution of the illuminant[4] used in the photoelectric instrument, T_r, T_g and T_b are, respectively, the spectral transmissions of the "red," green, and blue filters (together with spectral transmission of the glass optics), and S is the relative spectral response of the photo-cell. A geometrical constant of the instrument has been "absorbed" into the constants k_x, k_y, and k_z.

Since it is exceedingly improbable that a filter having the required spectral transmission T_r could be made, an additional filter[1] would be required in practice. The instrumental X would be obtained by employing this additional filter having spectral transmission $T_{rb}=k_{xb}T_r$ in the wave-length range of 0 to about 504 millimicrons, and $T_{rb}=0$ for wave-lengths in excess of 504 millimicrons, and a filter satisfying the requirement, $T_{rr}=T_r$ for all wave-lengths in excess of 504 millimicrons, and $T_{rr}=0$ for all wave-lengths less than 504 millimicrons. The constant k_{xb} is introduced to permit the use of a fourth filter having correct relative spectral transmission and incorrect magnitude. The instrumental X would then be given by the equation,

$$X=(k_x/k_{xb})\int_0^{504} E'RT_{rb}S\,d\lambda+k_x\int_{504}^\infty E'RT_{rr}S\,d\lambda. \tag{3}$$

Substituting photo-currents (in arbitrary units) for the integrals, we obtain

$$X=(k_x/k_{xb})i_{rb}+k_xi_{rr}, \quad Y=k_yi_g, \quad Z=k_zi_b. \tag{4}$$

We now imagine that reflectance measurements are made with the "red" filter (rr), the green filter (g), the blue filter (b), and the fourth, blue filter (rb), and that the reflectance values obtained are R_{rr}, R_g, R_b, and R_{rb}. If the four photo-currents which obtain when magnesium oxide is placed over the sample opening are, for the respective filters, I_{rr}, I_g, I_b, and I_{rb}, then, on the customary assumption that reflectances are referred to that of magnesium oxide taken equal to unity (or, in practice, 100 percent), the photo-currents appearing in Eqs. (4) can be replaced to obtain Eqs. (5).

$$X=(k_x/k_{xb})I_{rb}R_{rb}+k_xI_{rr}R_{rr}, \quad Y=k_yI_gR_g, \quad Z=k_zI_bR_b. \tag{5}$$

If the integrals which determine the photo-

[4] The light source is usually a tungsten filament lamp. In view of the rather complex form of the relative spectral energy distributions of I.C.I. standard illuminants B and C, the writer feels that emphasis should be given to the possibility of using two sets of filters in series, the first easily interchangeable and having the purpose of converting the spectral energy distribution of the light source to any of the I.C.I. standard illuminants; it should then be simpler to design the second set of filters, and the colorimeter would have a greater range of usefulness. If the first filters were placed between the light source and the sample, and the second filters between the sample and photo-cell, errors due to fluorescence phenomena would be removed.

currents I_{rb}, I_{rr}, I_g, and I_b are substituted in Eqs. (5), we obtain for the instrumental tristimulus values,

$$X=k_x\left\{\left[(1/k_{xb})\int_0^{504}E'T_{rb}S\,d\lambda\right]R_{rb}+\left[\int_{504}^{\infty}E'T_{rr}S\,d\lambda\right]R_{rr}\right.,$$
$$Y=k_y\left[\int_0^{\infty}E'T_gS\,d\lambda\right]R_g, \tag{6}$$
$$Z=k_z\left[\int_0^{\infty}E'T_bS\,d\lambda\right]R_b.$$

Substituting for k_x, k_{xb}, k_y, and k_z, we obtain

$$X=\left[\int_0^{504}E\bar{x}\,d\lambda\right]R_{rb}+\left[\int_{504}^{\infty}E\bar{x}\,d\lambda\right]R_{rr},$$
$$Y=\left[\int_0^{\infty}E\bar{y}\,d\lambda\right]R_g, \tag{7}$$
$$Z=\left[\int_0^{\infty}E\bar{z}\,d\lambda\right]R_b.$$

The writer has advisedly used several steps in the deduction of Eqs. (7) for the relationships between tristimulus values and instrumental reflectances, because the evaluation of the coefficients in the equation for X has proved confusing. Normalizing the spectral energy distribution of the illuminant E, so that Y will be visual efficiency (or R_g), and abbreviating, we have,

$$X=m(aR_{rr}+bR_{rb}),\quad Y=R_g,\quad Z=nR_b. \tag{8}$$

Gibson[1] gives the values, $a=0.83$ and $b=0.17$, these values being respectively the ratios of the areas under the $\bar{x}$ curve from 504 millimicrons upward and 504 millimicrons downward, to the total area under the curve. While the (standard) illuminant for these values is not given, it is apparent from Eqs. (7) that $a=0.83$ and $b=0.17$ only when $E=$ const., that is, when the illuminant has equal energy distribution. When the I.C.I. standard illuminant C is used, $a=0.799$ and $b=0.201$, or, with sufficiently good precision, $a=0.8$ and $b=0.2$; also, $m=0.98$ and $n=1.18$, m and n being tristimulus values for magnesium oxide.

Emphasis should be given to the consideration that a photoelectric colorimeter would yield accurate color specification only when its filters (with regard for the spectral transmission of the glass optics) are so designed that, at each wave-length, $T_{rr}=$(const.)$E\bar{x}/E'S$, except for wave-lengths below 504 millimicrons where $T_{rr}=0$, $T_{rb}=$(const.)$E\bar{x}/E'S$, except for wave-lengths above 504 millimicrons where $T_{rb}=0$, $T_g=$(const.)$E\bar{y}/E'S$, and $T_b=$(const.)$E\bar{z}/E'S$. If the filters of the photoelectric colorimeter do not accurately satisfy these requirements (or the more difficult requirements of Eqs. (2)), it would appear that the colorimeter could not serve generally either for color specification or color matching, but would be strictly limited to applications where spectrophotometric data indicate that it would be permissible to control or match colors by holding constant the three or four reflectances obtained with filters which pass broad portions of the spectrum.

III. Chromaticity Limitations and Errors of the Three-Filter Photoelectric Colorimeter

Because of the similarity in form of the $\bar{x}$ distribution function for wave-lengths less than 504 millimicrons to that of the $\bar{z}$ distribution function, it has been suggested that the blue filter, correctly designed to have spectral transmission T_b, might be used in practice in place of the fourth filter having spectral transmission T_{rb}. With the exception of the hypothetical three-filter instrument having filters which satisfy the difficult requirements of Eqs. (2), a three-filter instrument would seem to be most nearly perfect when its three filters have spectral transmissions T_{rr}, T_g and T_b, the third or blue filter serving both for the measurement of R_b and R_{rb}.[5] It is of interest to investigate the chromaticity limitations and errors of this best physically realizable three-filter photoelectric colorimeter.

Equations (8) giving the instrumental tri-

[5] On the basis of the assumption that a filter having the required spectral transmission T_r cannot be made, the phrase used in this paper, "best physically realizable three-filter photoelectric colorimeter," should be taken to mean a colorimeter equipped with three filters having spectral transmissions T_{rr}, T_g, and T_b, respectively.

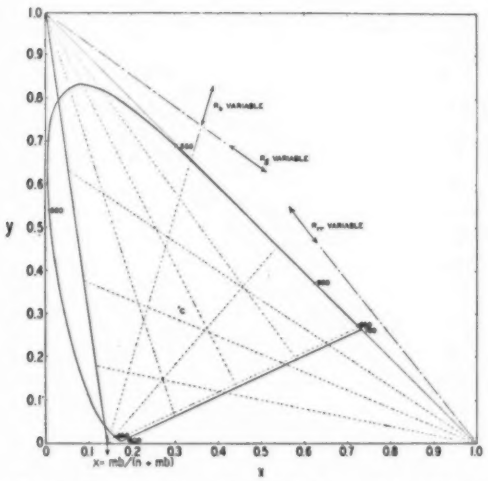

FIG. 1. When points on the I.C.I. chromaticity diagram determined by the physically realizable three-filter photoelectric colorimeter are displaced due to variation in, (*i*) the "red" reflectance R_{rr} alone, (*ii*) the green reflectance R_g alone, and (*iii*) the blue reflectance R_b alone, the displacements lie on straight lines passing, respectively, through (*i*) the point, $x=1$, $y=0$, (*ii*) the point, $x=0$, $y=1$, and (*iii*) the point, $x=mb/(n+mb)$, $y=0$; displacements due to errors in X resulting from use of R_b in X lie on straight lines of family (*i*). All possible points obtainable with the best physically realizable three-filter photoelectric colorimeter are restricted to that (greater) part of the chromaticity diagram lying to the right of the line connecting $x=0$, $y=1$ and $x=mb/(n+mb)$, $y=0$.

stimulus values, now become

$$X=m(aR_{rr}+bR_b), \quad Y=R_g, \quad Z=nR_b. \tag{9}$$

It is convenient to develop relations which describe how a point on the I.C.I. chromaticity diagram is displaced when two reflectances are held constant and the third reflectance is varied. The trichromatic coefficients,

$$x=X/(X+Y+Z), \quad y=Y/(X+Y+Z), \quad z=Z/(X+Y+Z), \tag{10}$$

may be expressed as functions of the instrumental reflectances by substitution from Eqs. (9). When the trichromatic coefficients are so expressed, and R_{rr}, R_g, and R_b are successively eliminated, the following relationships between x and y for R_{rr} variable (Eq. (11)), R_g variable (Eq. (12)), and R_b variable (Eq. (13)) are obtained:

R_{rr} variable $$y=\frac{R_g}{R_g+nR_b}(1-x), \tag{11}$$

R_g variable $$x=\frac{m(aR_{rr}+bR_b)}{m(aR_{rr}+bR_b)+nR_b}(1-y), \tag{12}$$

R_b variable $$y=\frac{(n+mb)R_g}{m(naR_{rr}-bR_g)}\times\left(x-\frac{mb}{n+mb}\right). \tag{13}$$

Referring to Fig. 1, Eq. (11) is represented by a family of straight lines, all of which pass through the point $x=1$, $y=0$ (an unreal primary of the I.C.I. system). If, for a given pair of correct values R_g and R_b, R_{rr} is in error, the displacement of the instrumental point on the chromaticity diagram from the correct point will lie on one of this family of straight lines. Eq. (12) is represented by a family of straight lines passing through the point $x=0$, $y=1$ (a second unreal primary). A displacement of an instrumental point due only to error in R_g will lie on one of this family of lines. Inspection of Eq. (13) shows that displacements of instrumental points due to errors in R_b fall on straight lines which pass through the point $x=mb/(n+mb)$, $y=0$ (and not through the third unreal primary $x=0$, $y=0$, because a change in R_b produces a change in both Z and X).[6]

The limiting lines of the family passing through $x=1$, $y=0$ are the x axis and the straight line connecting $x=1$, $y=0$ and $x=0$, $y=1$; this means that the family for R_{rr} variable covers the whole chromaticity diagram. It is found, however, that the families for R_g variable, and R_b variable do not cover the whole chromaticity diagram. The limiting lines for the family R_g variable are the line connecting $x=1$, $y=0$ and $x=0$, $y=1$, and the line connecting $x=0$, $y=1$ and $x=mb/(n+mb)$, $y=0$, the latter point being that through which the family of lines for R_b variable passes. The family of lines for R_b variable are confined between the line passing through $x=0$, $y=1$, and the positive x axis. We note, therefore, a fundamental limitation imposed on chromaticities given by the type of three-filter photoelectric colorimeter under dis-

[6] Visualization of the straight lines graphically representing equations like 11, 12, 13 involving X, Y, Z are of help in qualitative discussion of the relationship between a change in a spectrophotometric curve and the corresponding chromaticity change.

cussion: no combination of *possible* reflectances can place a point in that part of the chromaticity diagram which lies between the line connecting the points $x=0$, $y=1$ and $x=mb/(n+mb)$, $y=0$, and the y axis.[7] When the I.C.I. illuminant C is assumed, the point on the x axis is at $x=mb/(n+mb)=0.1425$, a very appreciable distance from the origin. It is immediately apparent that the instrumental points on the diagram for colors whose true chromaticities are represented by points in the excluded region will fall to the right of the limiting line. It will also be seen that the directions of the displacements from the true points will be toward the point $x=1$, $y=0$, for Eq. (11) can be written,

$$X \text{ variable} \qquad y=\frac{X}{Y+Z}(1-x). \tag{14}$$

Assuming that Y and Z are correct, X may be in error because of the fundamental error involved in assuming that R_{rb} may be replaced by R_b, or the error in X may be a combination of the difference between R_b and R_{rb} and error in R_{rr}; in either case, Eq. (14) informs us that the displacements of instrumental points from true points will lie on straight lines passing through the point $x=1$, $y=0$.

Approximate maximal chromaticity errors having origin in the assumption that

$$X=m(aR_{rr}+bR_b)$$

are represented by straight line segments on the chromaticity diagram of Fig. 2, for which illuminant C was assumed. These segments are given for a number of correct points, designated with open circles, representing chromaticities having 100, 50, and 0 percent excitation purities. The maximal variations of the instrumental points (toward and away from the point $x=1$, $y=0$) from given, correct points were established by calculation of tristimulus values of hypothetical reflectors having spectral reflectance $R=0$ except at one or more properly chosen wave-lengths at which, in a 1 millimicron range, the reflectance rose discontinuously to high arbitrary, but properly weighted, values. The ideal Eqs. (8) were used to establish suitable

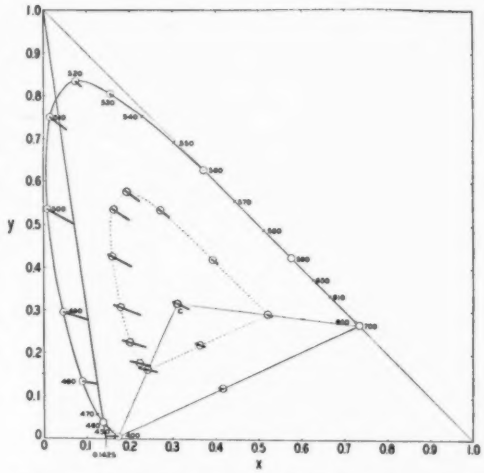

FIG. 2. Approximate maximal displacements, represented by segments of straight lines, of chromaticities determined by the best physically realizable three-filter photoelectric colorimeter from corresponding correct chromaticities, represented by open circles. Note that instrumental points corresponding to points on the spectrum locus are displaced to, and beyond, the limiting line (see Fig. 1). For actual samples, the displacements would usually be considerably smaller than those given on the diagram, but objectionably large for certain colors of importance, the magnitudes of the displacements depending on form of the spectrophotometric curves. The 50 percent excitation purity locus is represented by the dotted curve.

hypothetical spectral reflectance for each of the several points, and instrumental tristimulus values were calculated by means of Eqs. (9), with $m=0.98$, $a=0.80$, $b=0.20$, and $n=1.18$.

It will be seen that the maximal chromaticity errors are greatest for the hypothetical reflectors having dominant wave-lengths in the neighborhood of 500 millimicrons. This is attributed to the fact that the $\bar{z}$ function departs seriously from the function $c\bar{x}$ in the neighborhood of 500 millimicrons (c being a constant so chosen that the $\bar{x}$ and $\bar{z}$ functions "fit" as well as possible in the approximate wave-length range, 400 to 500 millimicrons).

While the magnitudes of chromaticity errors indicated on the diagram of Fig. 2 are enormous as compared with least perceptible chromaticity differences,[8] it must be emphasized that spectrophotometric curves rarely exhibit very sharp peaks and that, as a consequence of this, most instrumentally determined chromaticities will be

[7] However, samples having color sufficiently saturated to fall within this region would be rare.

[8] D. B. Judd, J. O. S. A. **26**, 421 (1936).

in error by amounts considerably less than the theoretical maximal errors. Depending on the nature of the spectral reflectance curve, the instrumentally determined point for a given chromaticity (not in the excluded region) may lie anywhere on the segment constructed through the given point, and, indeed, there will be cases for which the instrumental point will nearly coincide with the correct point, these cases occurring when the spectrophotometric curves are of such form that, very nearly, $R_b=R_{rb}$. In the absence of spectrophotometric data, however, one would be in ignorance of the validity of the assumption that $R_b=R_{rb}$; attention must be given to the fact that the spectrophotometric curves of many important colors exhibit large slopes and strong curvatures in the wave-length range covered by the $\bar{z}$ distribution function. Chromaticity errors may be estimated with the help of Eqs. (15), which are derived from Eqs. (10).

$$\begin{aligned}\delta x &= x[(1-x)(\delta X/X)-y(\delta Y/Y)\\ &\qquad -z(\delta Z/Z)],\\ \delta y &= y[-x(\delta X/X)+(1-y)(\delta Y/Y)\\ &\qquad -z(\delta Z/Z)],\\ \delta z &= z[-x(\delta X/X)-y(\delta Y/Y)\\ &\qquad +(1-z)(\delta Z/Z)].\end{aligned} \tag{15}$$

The fractional errors in the tristimulus values may be obtained from errors in reflectance through Eqs. (9). It is interesting to note, in passing to the application of the error equations to the present discussion, that these equations indicate, fairly generally, that errors in reflectance must not be larger than about 0.003 (depending, of course, on the tristimulus values), where one or two of the three reflectances are correct and it is desired to keep δx and δy less than, say, 0.001. While this rather rigid restriction on instrumental accuracy is known to those working in the field of colorimetry, it seems not to be appreciated by a number of the designers of existing photoelectric instruments.

Since we have taken the best physically realizable three-filter photoelectric colorimeter, $\delta Y=0$, $\delta Z=0$, and δX exists only because it has been assumed that the blue filter can serve for both its normal purpose and for the measurement of R_{rb}. If the difference R_b-R_{rb} is abbreviated to δR, then the fundamental error in X is, according to Eqs. (9), $\delta X=mb\delta R$. Eqs. (15) become

$$\begin{aligned}\delta x &= \frac{x(1-x)}{(a/b)R_{rr}+R_b}\delta R,\\ \delta y &= \frac{-xy}{(a/b)R_{rr}+R_b}\delta R, \quad \delta z=-(\delta x+\delta y).\end{aligned} \tag{16}$$

Since the displacements of instrumental points on the chromaticity diagram from corresponding correct points are on straight lines having slopes equal to or less than unity, δx is equal to or greater than δy. Partly because of this, and partly because of the nature of ellipses on the chromaticity diagram which Judd[8] presents for the estimation of chromaticity differences, δx is more representative of the chromaticity differences associated with the instrumental error under discussion than is δy. According to the diagram which Judd presents for estimation of chromaticity differences, the number of least perceptible differences per unit distance on the I.C.I. diagram varies quite widely over the diagram. A fairly typical figure is 0.0005 per least perceptible difference, in the direction of the x axis. Arbitrarily taking twice this distance, we obtain 0.001, a figure which is often used in connection with practical work. Imposing the somewhat arbitrary condition that δx be less than 0.001, and substituting the value $a/b=4$ for illuminant C, we obtain a criterion that the instrument have chromaticity sensibility of the same order as that of a normal observer:

$$\delta R \lessapprox \frac{0.001(4R_{rr}+R_b)}{x(1-x)}. \tag{17}$$

The inequality (17) states that the permissible upper limit for δR is a function only of the "red" reflectance, R_{rr}, the blue reflectance, R_b, and the trichromatic coefficient, x.

We should expect to find the instrumental errors rather large where R_{rr} and R_b are small, with the spectral reflectance curve exhibiting a steep positive slope in the neighborhood of 450 to 500 millimicrons, that is, where the colors are typical blue-greens and greens. We may take, as typical values, $R_{rr}=13$ percent, $R_b=18$ percent, $x=0.23$; according to inequality (17), δR must

then be less than about 0.4 percent reflectance unit. Integrations performed to obtain R_b and R_{rb} show that $\delta R = R_b - R_{rb}$ is typically 2 to 3 percent reflectance units; for unusually high excitation purities, δR would be considerably greater than this. The instrument would fail to give sufficiently accurate color specification for many other colors of importance; for many yellows, δR could permissibly be as large as about 1.5 percent, but many yellows of importance could be found for which δR would be appreciably in excess of this value. We must conclude that the specification of color by the best physically realizable three-filter photoelectric colorimeter would often be seriously in error.[9]

It would seem that such an instrument might validly be used for the specification of color of the "whites."[10] A typical permissible value for δR would be 1.5 percent. Since the slopes of the spectrophotometric curves of most whites, particularly high whites, are small in the region of the spectrum covered by the $\bar{z}$ distribution function, δR would usually be considerably less than 1.5 percent, and the instrument would yield sufficiently accurate color specification. Even with whites, however, one must proceed with caution and test the validity of application of the instrument with spectrophotometric data. As an illustration, the spectrophotometric curves of pulp and paper are of such a nature as to make δR of the order of 1.5 percent.

We have seen that, for a given point on the chromaticity diagram, the corresponding instrumental point may fall anywhere on a short segment of a straight line through the given point and the point $x=1$, $y=0$, the displacement of the instrumental point from the correct point depending upon the nature of the spectrophotometric curve. Hence, if two samples have the same chromaticities but dissimilar spectrophotometric curves, the instrumental chromaticities would, in general, be different; in other words, if two samples constitute a color match to the I.C.I. standard observer under a standard illuminant, the instrumental chromaticities (for the same illuminant) would, in general, be different. Conversely, it does not necessarily follow that a true color match (for the given standard illuminant) exists when the three reflectances for the two samples are respectively the same. These comments hold for the best physically realizable three-filter photoelectric colorimeter; in most existing three-filter photoelectric instruments *any* red filter (usually literally red—the color should be yellow[1]), *any* green filter, and *any* blue filter are used (in the case of one instrument, the transmission of the blue filter was found to be appreciable over the whole visible spectrum and over that part of the near infrared to which the photo-cell was responsive). It is difficult to estimate generally how bad are color matches indicated by most of the existing three-filter photoelectric instruments; certainly, in many cases, they would be unsatisfactory.

[9] Gibson, reference 1, warns that one desirous of obtaining as high accuracy as obtainable with spectrophotometric data would probably be disappointed.

[10] Gibson, reference 1, points out this possible application.

Improved Diffraction Patterns

MASON E. HUFFORD
Indiana University, Bloomington, Indiana
(Received June 14, 1937)

By means of apparatus of unusual dimensions and a method of producing monochromatic light of exceedingly narrow range of wave-length, improved diffraction patterns have been produced. The photographs show much greater detail than is usual. An exceptional pattern produced by a square opening is shown.

THE diffraction of light and the resulting pattern of fringes have always been of interest to physicists. For some years the author has experimented in the photography of diffraction patterns and in the improvement of methods whereby the system of fringes may best be produced.

Some rather unusual diffraction patterns have resulted from this study.[1]

[1] Phys. Rev. **3**, 241 (1914); **7**, 545 (1916); **33**, 589 (1929).

It has seemed to the writer that the photography of the more important of the usual diffraction fringe systems could be greatly improved in detail. This paper is a result of such an attempt. The patterns represent a number of fringes and a contrast which has not heretofore been reached. The paper also presents a new pattern, Fig. 1, which it appears has not been published before.

A large number of inquiries regarding the work already published and an interest expressed by

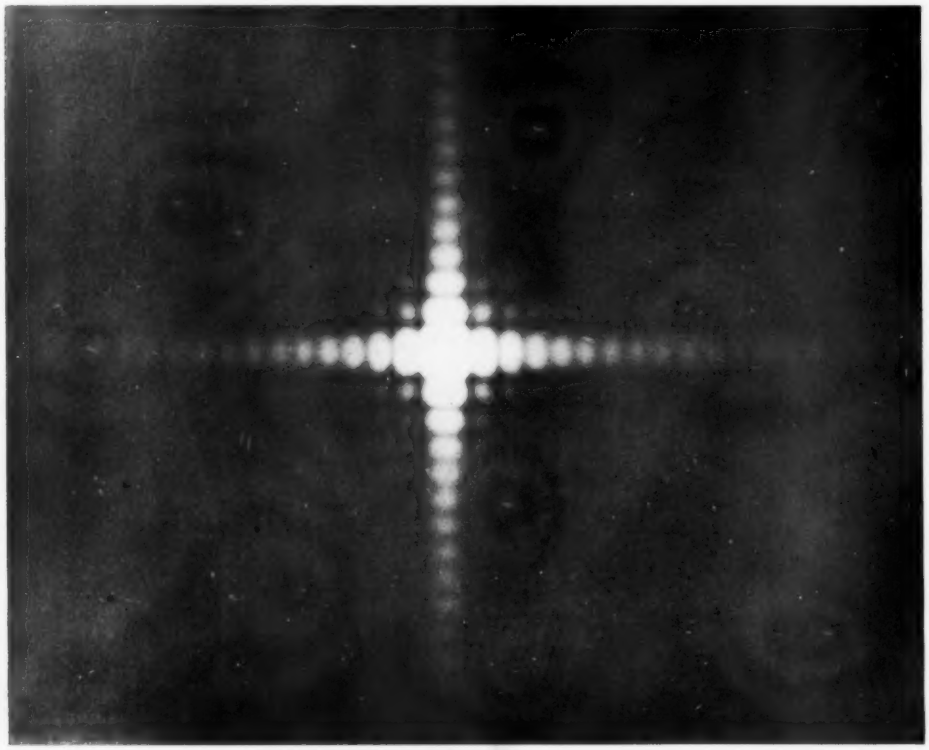

FIG. 1.

many physicists in the patterns here shown have suggested the publication of these photographs.

The success of this work results from the use of unusual apparatus available for this study. The diffraction tube is a light tight box of metal, 14 in. by 14 in. and 110 feet long. The image of the positive carbon of a right angle arc lamp was focused on the slit of a spectrometer and the light dispersed into its spectral colors by a sixty degree prism. The lamp was supplied with 30 amp. d.c. current. With the eyepiece of the spectrometer replaced by a tube which was closed at the end by a metal plate carrying a circular hole 0.41 mm in diameter, the light of wavelength 3880A passed down the diffraction tube. This arrangement[2] has proved unsurpassed for the production of monochromatic light. The intensity of the light is low but the range of wave-lengths admitted is but a few angstroms.

Diffraction objects were placed at the midpoint of the tube and the photographic plate at the farther end. Photographic plates of very fine grain were used. Cramer No. 25 and Eastman Kodalithic proved best. Exposures were from five to ten hours.

Figure 1 represents the system produced by diffraction through a rectangular opening. The square opening, $1\frac{1}{2}$ mm by $1\frac{1}{2}$ mm was formed by overlapping carefully worked pieces of brass. On the original plate as many as eighteen bright fringes can be seen. It will also be observed that in each quadrant appears a system of fringes formed by the combined effect of two straight edges at right angles to each other. This checkerboard pattern has been discussed and illustrated in textbooks by drawings.[3] However a photograph of the pattern seems not to have been published.

[2] Phys. Rev. **7**, 545 (1916).

[3] R. W. Wood, *Physical Optics* (1934), p. 239.

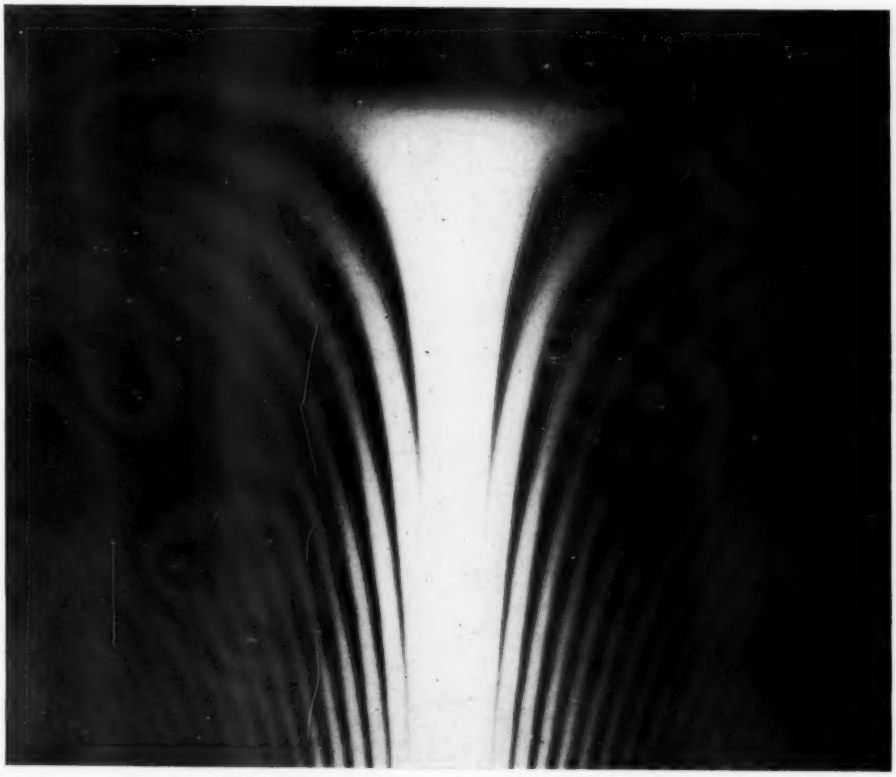

FIG. 2.

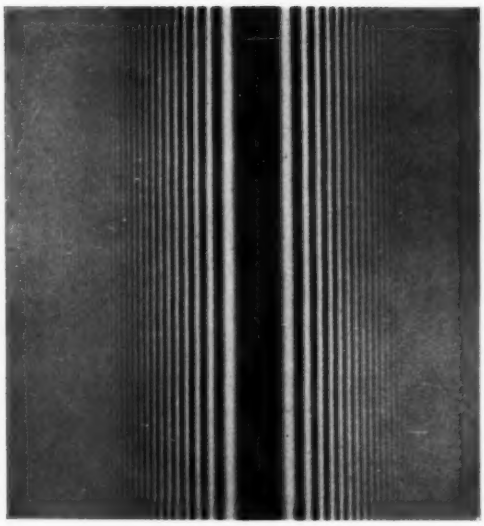

FIG. 3.

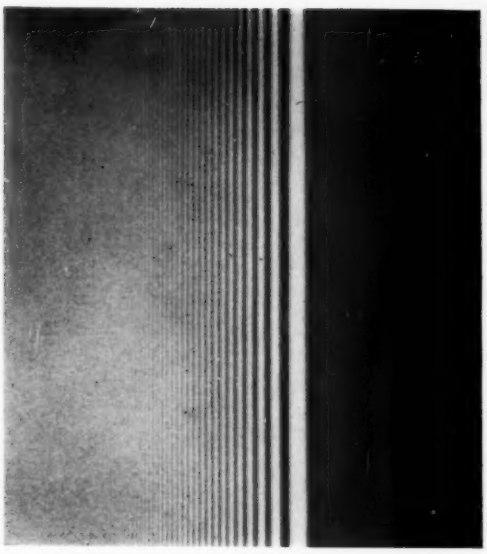

FIG. 4.

Figure 2 is the pattern produced by monochromatic light passing through a wedge shaped opening. A similar pattern has been published by Franklin.[4] However it will be seen that the pattern produced under the conditions of this experiment shows very many more fringes. The opening used for Fig. 2 was formed of pieces of brass with edges ground smooth and polished. It tapered from $2\frac{1}{2}$ mm at the bottom to a point at the top and was 6 cm long.

Figure 3 is the diffraction pattern produced by a fine wire, 0.3 mm in diameter. The interest in this pattern is the exceptional number of fringes which appear on either side of the center of the pattern. It will be seen that the bright band at the center of the geometric shadow is apparent.

Figure 4 is the pattern produced by a straight edge. On the original plate as many as forty dark fringes can be counted. In the right half of the photograph the illumination falls off gradually in the direction of the geometric shadow. Other photographs show this decrease of intensity spread over a wider region but in such cases the diffraction fringes are broader with a sacrifice of any considerable number of them.

[4] Franklin, Phys. Rev. **14**, 61 (1902).

An Improved Spectroradiometric Method and Apparatus for Measuring Small Polarization Ellipticities

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(Received September 11, 1937)

A modification of the Sénarmont-Chauvin compensator for measuring small polarization ellipticities has been applied to spectroradiometric work. Over the larger share of the usable spectral range of 0.6μ to 2.0μ the sensitivity is in a class with the best visual methods, and by some sacrifice of spectral purity may be made much more sensitive than any other known method. It has been applied in measuring the Kerr dispersion of CCl_4, which is found to follow the Havelock law very closely.

THE method used by W. R. Winch[1] and the writer in making ellipticity (e.g., Kerr) measurements in the early infrared spectral region has certain marked disadvantages. It is, in effect, a direct comparison of the two axes of the ellipse, and as the intensity or energy measurements are proportional to the *squares* of these axes it is evident that small ellipticities are very difficult or impossible to measure in this way. As a matter of fact the smallest phase change so measurable is of the order of 1°, putting this method as regards accuracy in a class with the ordinary Babinet compensator.

In seeking for a method applicable to smaller phase differences the writer made use of the following scheme:[2] The ellipse (Fig. 1) is reduced to the plane vibration CC' by a quarter-wave plate with axis in the line, e.g., AA'. By turning the $\lambda/4$ plate through 90° to BB' the plane vibration is shifted through the angle 2α to DD'. This means that a phase change, or the resulting ellipticity, is measured in terms of a *rotation* of plane of polarization. Now the writer's spectroradiometric method[3] and apparatus for measuring rotation of the plane of polarization of plane polarized radiation is capable of working with rotations smaller than a single minute of arc, and accordingly it should be possible to measure in this way polarization ellipses so thin that the ratio of axes is of the order of 1 : 10,000. The workable spectral range would be from less than 0.6μ to over 2.0μ.

To test the possibilities of this method measurements to determine the dispersion of the electro-optic Kerr effect were made on carbon tetrachloride. This material has a Kerr constant less than 1/40 that of carbon disulphide or 1/4000 that of nitrobenzene and would be quite impossible to work with by the method first mentioned. It was contained in a Pyrex cell with chromium-plated brass plates 3×47×90 mm, 7 mm apart. A transformer and kenetron potential source gave a field of approximately 25,000 volts/cm.

The radiation source was a tungsten strip filament lamp L (Fig. 2), whose light was concen-

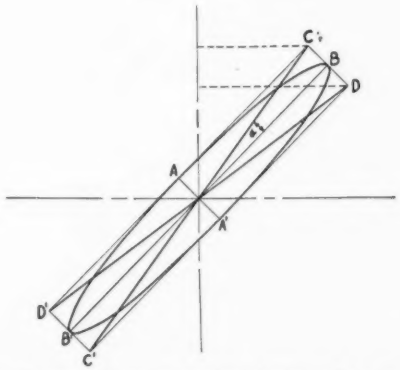

FIG. 1. Diagram illustrating the principle of the method.

[1] L. R. Ingersoll and Wesley R. Winch, Phys. Rev. **44**, 399 (1933).

[2] As described here this method is essentially that of Sénarmont-Chauvin applied to spectroradiometric work. It is, however, as will appear later, actually used in a somewhat different way. See A. Cotton and H. Mouton, Ann. Chim. Phys. **11**, 159 (1907); **19**, 158 (1910); J. de phys. **1**, 8 (1911). W. Schutz, *Handbuch der Experimentalphysik* Vol. 16–1, *Magnetooptik* (Akad. Verlagsgesellschaft, Leipzig, 1936), p. 223. For a general discussion of phase change measuring devices (compensators) see also G. Szivessy, *Handbuch der Physik*, Vol. 19 (Julius Springer, 1929), pp. 917–972.

[3] For references see L. R. Ingersoll, J. O. S. A. **5**, 157 (1921).

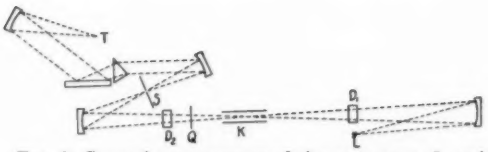

FIG. 2. General arrangement of the apparatus. L, strip filament tungsten lamp; D_1, D_2, double image prisms, set at 45°; K, Kerr cell; Q, mica quarter-wave plate; T, thermopile.

trated by a spherical mirror into a narrow conical beam, polarized by passage through a large double-image prism D_1 (only one image being used), with principal plane at 45° azimuth, passed between the Kerr plates K, through the $\lambda/4$ plate Q and second double-image prism D_2, and then concentrated on the slit S. The second double-image prism D_2 was of the Wollaston type, and both images were used. Its principal planes were vertical and horizontal, i.e., at 45° with that of D_1, and with Q removed and K not excited the two images formed on S were practically equal in intensity. They were close together and vertically one above the other. A system of sliding needle points in front of the slit served to increase or diminish the intensity of either image slightly, and thus balance exactly the two intensities when desired. The polarizing prism D_1 and $\lambda/4$ plate Q were mounted in massive conical brass bearings carrying divided circles.

The light from these two images passed through the mirror spectrometer and concentrated in two spectra on the two arms of a special compensating thermopile T, so connected that when the spectral intensities were the same (for the wave-length on the thermopile receiving strips) there was no galvanometer deflection. The thermopile consisted of four bismuth-tellurium couples with thin blackened gold receiving surfaces 0.6 mm×10 mm, mounted, of course, in line and vertically one above the other. It was used in a high vacuum, maintained by a charcoal trap in liquid air. The galvanometer was a Zc (Kipp and Zonen).

To provide the necessary series of quarter-wave plates—one for each wave-length—a large number of 5 cm square sheets of the highest grade optical mica[4] of thickness varying from 0.03 mm to 0.12 mm were first tested by eye for uniformity between crossed Polaroid plates[5] and then mounted in succession in the divided circle at Q. With D_1 and D_2 set parallel and the mica with axis at 45° the galvanometer deflection would evidently be zero for the particular wave-length for which the mica was a $\lambda/4$ plate (or, of course, a $3/4\lambda$ plate), for the resulting circularly polarized beam would have equal components.

To measure ellipticities it is evident that there had to be some means of interpreting the galvanometer deflection[6] resulting from the azimuth rotation 2α so as to allow measurements of this angle. To do this the polarizing prism D_1 was turned from its 45° azimuth through a small angle—about 4°—(rotating the $\lambda/4$ plate Q at the same time so that its axis remained parallel to D_1 and hence would not affect the beam) and the galvanometer deflection—using sensitivity-reducing shunts—measured and compared with that resulting from the ellipticity measurements.

The procedure then in making Kerr (or other ellipticity) measurements was very simple. A suitable mica lamina was mounted at Q with its plane parallel to D_1 (45° azimuth) and the spectrometer set for the wave-length for which this was an exact quarter-wave plate. On exciting the Kerr cell an elliptical vibration was produced which was rendered plane again by Q, and as Q was rotated between 90° stops this plane would rotate through 2α and give a corresponding galvanometer deflection which was compared with that produced by a direct 4° rotation as just described. The ratio of the ellipse axes is evidently given by tan α and α can be readily shown (see reference 1, p. 400) to be equal to $\delta/2$, where δ is the phase change producing the ellipse.

As a matter of fact, in measuring very minute Kerr or other phase changes the matter is complicated by inevitable small birefringence in the cell ends or other parts of the system. To avoid this complication a somewhat different technique was used whereby Q was not rotated 90° but rather the galvanometer deflection measured

[4] From Eugene Munsell and Co., New York. A mica quarter-wave plate for wave-length 1μ is approximately 0.05 mm thick; for 2μ, 0.11 mm thick.

[5] Polaroid plates could be not used as polarizers in the main part of this work since their polarizing property is sharply limited to the visible spectrum. See L. R. Ingersoll J. G. Winans, and E. H. Krause, J. O. S. A. **26**, 233 (1936).

[6] It is almost self-evident that this deflection will be proportional to the rotation of the plane of polarization, if this is small. For the simple theory see L. R. Ingersoll, Phys. Rev. **23**, 489 (1906).

when the potential across the plates was turned on and off. If there was no secondary birefringence it is evident that this process would effectively give α. As a matter of fact, it measured instead the *additional birefringence* (due to the Kerr effect) which is really what is wanted.

The results are shown in Fig. 3. The CCl_4 (Eastman) showed negligible conductivity and measurements were made at an average cell temperature of 26.0°C. The curve follows exceedingly well the Havelock[7] dispersion law

$$K = C(n^2-1)^2/n\lambda.$$

The two curves are fitted at $\lambda = 1.0\mu$.

Some study of errors has been made in connection with this method—the effect of lack of uniformity in the quarter-wave plate, of error in setting the axes, of the presence of a small amount of unpolarized light in the beam, and several others. So far as can be seen, each introduces in the phase determination an inaccuracy of not appreciably larger percentage than its own, and this, if necessary, can be corrected for. The most serious error under some circumstances results from the use of a slightly conical, i.e., not strictly parallel beam. This is, in general, necessary to secure sufficient radiation energy. While in most cases the difficulty it causes is negligible, it might introduce complications in the study of the Cotton-Mouton effect, i.e., magnetic birefringence. An attempt will be made to overcome this difficulty.

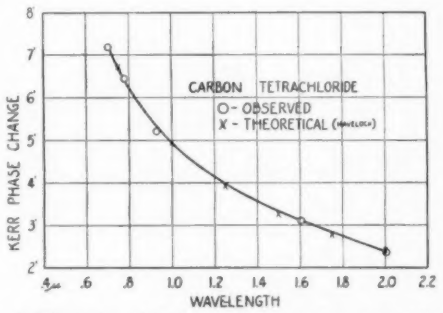

FIG. 3. Dispersion of the Kerr effect in carbon tetrachloride.

[7] T. H. Havelock, Phys. Rev. **28**, 136 (1909).

It is of interest to compare this method, as regards probable error, with some of the standard methods used in the visible spectrum. Because of the large variation of energy available in different parts of the spectrum, the probable error will vary considerably, but in the region of 0.8μ to 1.6μ the error in phase determination—always assuming that the total phase change is small—is probably about 0.2′. This, figured in the usual way, is $1\times10^{-5}\lambda$. Szivessy[2] lists the probable error of the Babinet compensator as from 7×10^{-3} to $1\times10^{-3}\lambda$, of the Brace compensator as 5×10^{-5} to $3\times10^{-5}\lambda$, and of the Rayleigh compensator as developed by de Forest Palmer as $5\times10^{-6}\lambda$. But while there is a more or less definite limit to the accuracy of any method dependent primarily on the human eye, there is no such limitation in spectroradiometric work. By a sacrifice of spectral purity, thereby increasing the available radiation flux, and by making use of such amplifying devices as the thermorelay, it is likely that the probable error for minute ellipticities could be reduced to as low as 1/100 of the value above mentioned. It is hoped that this high sensitivity will make this method immediately applicable to certain electro-optic and magneto-optic work which will be shortly attempted with it.

In conclusion, I wish to express my thanks to the Wisconsin Alumni Research Foundation for supporting this research. I also want to acknowledge my indebtedness to Mr. J. P. Foerst for his care and skill in making the thermopile and other delicate parts of the apparatus.

A Calculator for Obtaining Tristimulus Values from Spectrophotometric Data

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Chemistry Department, Purdue University, Lafayette, Indiana
(Received September 23, 1937)

THE development of recording spectrophotometers has increased the need for rapid methods of calculating tristimulus values for specifying color. The ideal method of making such calculations is represented, no doubt, by the integrating instrument developed by Hardy[1] which is driven by the spectrophotometer. Such a device is necessarily complicated and expensive.

The selected ordinate method described by Hardy and co-workers[2] greatly reduces the labor involved as compared to the older or weighted ordinate method. The procedure is simplified to the point that it consists in adding the transmission or reflection values for thirty selected wave-lengths for each primary and multiplying the sum of each by appropriate factors. For colors which do not differ greatly from white or gray, a system of ten selected ordinates is sufficient. Hardy has recommended the use of a glass plate ruled with the wave-lengths for a given primary as an aid in reading transmission or reflection values from a graph. The calculator to be described represents an extension of this idea and although no more accurate, eliminates the need of determining the numerical values at the selected ordinates along the curve. The use of this device requires that all spectrophotometric curves to be evaluated be drawn on the same size of graph paper.

The details of construction are shown by Fig. 1. The graph paper is held in a definite position on the base plate by means of clamps. A brass bar *a* has engraved on it the thirty selected wave-lengths for a given primary spaced so as to coincide with those on the graph paper. The bar can be moved from zero to 100 percent over the graph by means of two fine endless chains which pass over sprocket wheels. The top and bottom sprockets are each fastened to a shaft to maintain lateral alignment of the wave-length bar. The top shaft is connected to a revolution counter through a ratchet mechanism which allows the counter to revolve only when the wave-length bar is moved towards the bottom of the graph paper. The ratchet wheel contains 96 teeth and is engaged by four pawls spaced unequally with respect to the teeth. A tightener under the base maintains a constant tension on the chains. The lost motion in the mechanism is extremely small and error from this source is reduced further by the calibration. The revolution counter reads tenths of a revolution. An electromagnetic counter connected so as to add one each time the wave-length bar is brought down to zero is of considerable convenience in keeping a record of the number of points which have been added as one proceeds across the spectrum. There are three wave-length bars for each standard illuminant, one for each primary. These are interchangeable and are used in succession. The selected wave-lengths are given by Hardy.[2]

The procedure consists in moving the wave-length bar by means of the crank on the upper shaft to the point at which the first selected ordinate intersects the spectrophotometric curve *C*. The bar is then moved back to zero and the process repeated for the other ordinates. The process is continued for the bars for the other two primaries. The tristimulus coefficients can be calculated directly from the revolution counter readings without converting to any definite unit by multiplying by the factors given by Hardy[2] and reducing to a percentage basis. To obtain the brightness the instrument must be calibrated by noting the counter reading for ten or more movements of the wave-length bar from 100 to zero percent. The tristimulus values for the I.C.I. illuminant C can be calculated by means of the following equations:

$$X = \frac{\text{Counter reading} \cdot 0.03265 \cdot 10.0}{K},$$

$$Y = \frac{\text{Counter reading} \cdot 0.03333 \cdot 10.0}{K},$$

* Present address: E. I. duPont de Nemours and Co. Inc., Buffalo, N. Y.

[1] Hardy, J. Op. Soc. Am. **25**, 305 (1935).

[2] *Handbook of Colorimetry* (The Technology Press, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1936).

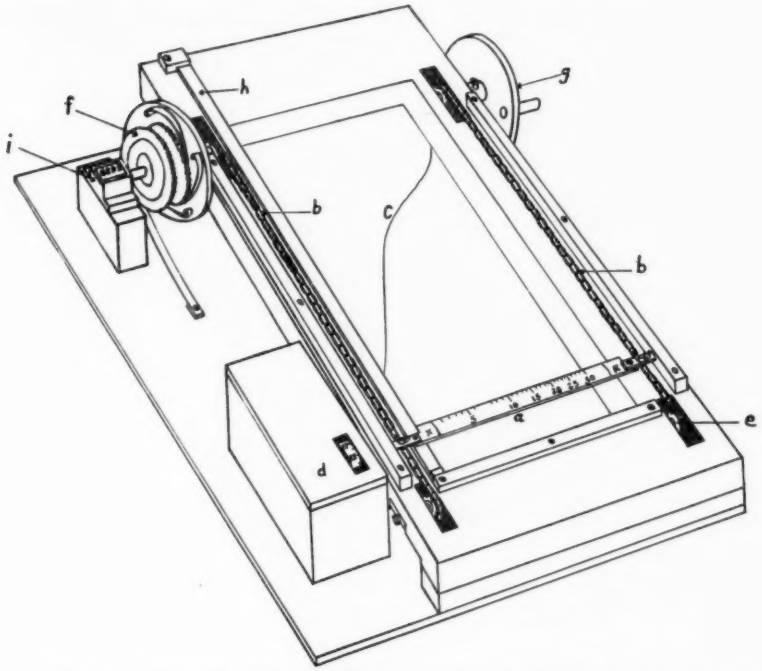

FIG. 1. *a*, Removable wave-length bar engraved with selected ordinates; *b*, fine endless brass chains; *c*, spectrophotometric curve; *d*, electromagnetic counter; *e*, brass sprocket; *f*, ratchet mechanism; *g*, wheel and crank; *h*, graph paper clamp; *i*, revolution counter.

$$Z = \frac{\text{Counter reading} \cdot 0.03937 \cdot 10.0}{K},$$

where K is the counter reading for ten movements from 100 percent.

This mechanical integrating device makes possible the calcualtion of the tristimulus values and the brightness for a color in about ten minutes. The tiresome reading of values from a graph is eliminated.

The Production of Large Single Crystals of Potassium Bromide Suitable for Optical Use

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George Eastman Research Laboratory of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received November 1, 1937)

AS reported earlier,[1] large single crystals of lithium fluoride are grown from the melt by lowering a pointed-bottom crucible containing the salt through a high temperature gradient region which embraces the freezing point. Due to the design of the furnace, shown schematically in Fig. 1, the melt and crystal are stored in regions of relatively low temperature gradient. The temperatures of these regions are such that vaporization of the melt is negligible and cracking of the crystal never occurs.

Because of the continued insistence of several infrared research workers the same general apparatus and method have been modified for the production of large potassium bromide single crystals suitable for optical use. Although several reports of potassium bromide crystallization had been published,[2-8] it was repeatedly pointed out that satisfactory crystals were not available. The modifications have been mostly in the direction of simplification and one or two of them may be regarded as improvements.

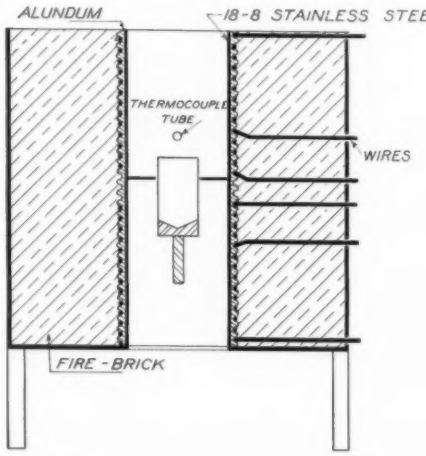


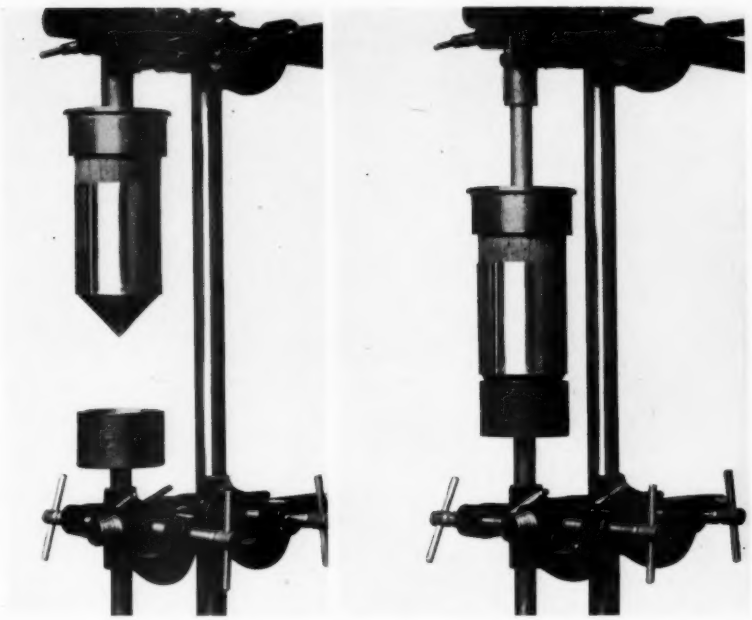
FIG. 1. Diagram of furnace cross section. In practice it is often convenient to use three separate windings in the upper furnace section to maintain a relatively low gradient therein.

Whereas commercial lithium fluoride salt was found to be unsuitable so that an elaborate method of synthesis had to be developed, potassium bromide of reagent quality can be crystallized from the melt with comparatively little difficulty. The salt, which is supplied in coarse granular form, is first roasted in a covered porcelain crucible until it no longer explodes and is then crushed to facilitate loading of the crucible.

Ninety degree conical bottom crucibles fabricated of 0.003 inch platinum sheet are supported by a stainless steel elevator of the type described earlier. Instead of turning out the dried alundum elevator lining to fit the cone, however, it has been found much more satisfactory to seat the crucible in wet alundum cement. The crucible is lightly forced into the cement, previously placed in the elevator, by means of a wooden plug turned to fit the crucible, the plug being guided by a brass rod which slides freely in a bearing whose axis coincides with that of the elevator. (See Fig. 2.) Tapping the bottom of the elevator with a small hammer causes all bubbles of appreciable size to rise to the top of the cement and effectively settles the cement around the crucible. After a day or two the cement is dry enough to heat without danger of cracking. This method has the advantages of allowing the use of imperfectly shaped cones such as result from repeated crystallizations and renders the careful spinning of cones unnecessary. It is applicable to the growth of other crystals as well.

As in the growth of lithium fluoride crystals, use is made of the high temperature gradient

[1] D. C. Stockbarger, R.S.I. **7**, 133 (1936).
[2] J. C. Slater, Proc. Am. Acad. **61**, 136 (1925).
[3] G. Tammann and G. Veszi, Zeits. f. anorg. allgem. Chemie **150**, 355 (1926).
[4] S. Kyropoulos, Zeits. f. anorg. allgem. Chemie **154**, 308 (1926).
[5] Gyulai, Zeits. f. Physik **46**, 80 (1927).
[6] P. W. Bridgman, Proc. Am. Acad. **64**, 19 (1929).
[7] K. Korth, Zeits. f. Physik **84**, 677 (1933).
[8] R. Hilsch, Angew. Chemie **49**, 69 (1936).



(*a*) (*b*)

FIG. 2. (*a*) The crucible is ready to be lowered into its seat. (*b*) The crucible is nearly seated. Tapping will complete the seating and cause the cement to rise to the shoulder.

which exists in the region between the upper and lower furnaces, but evidently the gradient requirements are not so severe. An annular baffle of sheet Nichrome, in place of polished platinum, is satisfactory.

The furnace temperatures are accurately regulated by means of the equipment developed earlier. A description of the method and apparatus is to be published in the *Review of Scientific Instruments*.

The procedure for loading the crucible is the same as for lithium fluoride, precautions being taken to prevent overheating of the salt at all times. After the initial loading of salt has melted, additions are made with the aid of a long stemmed Pyrex funnel. Crushed salt is preferred because there is less danger of splashing when it strikes the liquid. Spilling of salt in the furnace is to be avoided because of the resultant vaporization.

The crystallization process is begun with the bottom of the elevator in the plane of the baffle. The elevator is lowered by clockwork at the rate of 1 mm per hour, approximately, with the furnace temperatures set somewhat, say 25°C, below the normal initial values. This departure from normal is believed to aid in causing the growth of a single seed crystal. As soon as the top of the elevator has reached the baffle the temperatures are raised and are thereafter regulated in such a manner as to cause freezing to occur at that level at all times.

At the termination of the crystallization, the temperatures of both furnaces are brought to approximate equality somewhat below the melting point and the elevator is raised to the top of the upper furnace. The crucible with cover removed is lifted from its seat by special tongs and rested upside down on a thin piece of fire brick laid on the elevator. (See Fig. 3.) The elevator is quickly lowered to the bottom of the upper furnace and a second pair of special tongs is lowered to grasp the crucible near the cone. This pair of tongs is supported by an asbestos cord which runs over a pulley and which has on the other end a metal bar weighing a

FIG. 3. The crucible containing a crystal has been removed from its seat and is being placed upside down on a thin piece of fire brick laid on the elevator.

little less than the combination of tongs, crucible and crystal. (See Fig. 4.) The furnace currents are increased immediately to the extent that within a few minutes the crystal is melted loose from the crucible which is automatically carried to the top of the furnace by the action of the counter weight. The furnace currents are promptly decreased to a safe value and the crystal is cooled to room temperature after being released from the brick slab to which it becomes cemented by the small amount of molten salt which runs down during the melting-out process.

Melting the crystal loose is practiced because potassium bromide, unlike lithium fluoride, nearly always cracks into several pieces when left to cool in the crucible. Strong[9] has reported a somewhat similar procedure in which the entire furnace was inverted for melting out sodium chloride crystals.

Aside from an etching of the inside surface of the crucible near the top of the crystal, no depreciation of the platinum is noted. One crucible can be used repeatedly for a number of crystallizations. Leaks in the welded seams have been the only cause of life limitation so far. For this type of service a seamless spun crucible would be far better than those fabricated in the usual manner.

The crystals produced by the outlined method are clear and flawless. Clean cleavage surfaces after weeks of exposure to moist air in the laboratory are apparently as brilliant today as when first prepared. (See Fig. 5.) Likewise whole crystals retain their initial polish provided that they are not soiled during removal from the furnace. These observations suggest that properly handled prisms of artificial potassium bromide crystal material should not require elaborate methods of desiccation.

Inasmuch as this work was done to develop the method rather than to produce a stock of crystal material, no attempt was made to grow crystals larger than 5 cm in diameter by 7 cm in height. There is no apparent reason for ex-

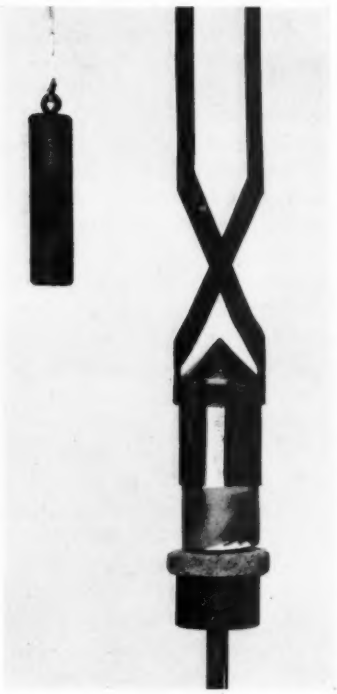


FIG. 4. The crystal is being melted loose. When entirely free, the crucible will be lifted by the counter weight to the top of the furnace.

[9] J. Strong, Phys. Rev. **36**, 1663 (1930).

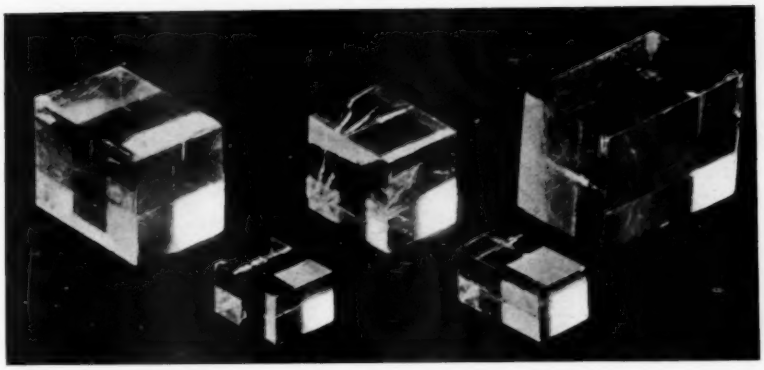


FIG. 5. Cleaved blocks of potassium bromide which have endured weeks of exposure during Boston's autumn rainy season. The only noticeable surface depreciation is in the form of scratches, the result of much handling. Refraction and internal reflection produced the checkered pattern.

pecting serious difficulty in the preparation of much larger potassium bromide crystals, particularly in view of the fact that a lithium fluoride crystal 11.5 cm in diameter has recently been grown.

Much of the apparatus used in this development was purchased with a grant from the Rumford Committee of the American Academy of Sciences to whom it is a pleasure to express gratitude.

The Optical Properties of Polaroid for Visible Light

MARTIN GRABAU
The Land-Wheelwright Laboratories, Inc., Boston, Massachusetts
(Received September 2, 1937)

THE transmission and polarization characteristics of Polaroid[1] have already been described in this journal, as well as elsewhere.[2] As far as I am aware, all the data in these reports were taken with material that was manufactured a year and a half or more ago. Routine research and the expansion of production during the past year have brought about such improvements in the optical properties of Polaroid that it seems worth while to publish an account of the current product.

The polarizing power of Polaroid resides in a thin film which is a set suspension of dichroic crystals, in substantially uniform orientation, in a cellulosic matrix. The film may be made in various thicknesses, usually between 0.001 and 0.004 inch. As the thickness of the film is increased, the transmission decreases and the degree of polarization of the transmitted light increases. In order to give the film stiffness and to protect it from damage, it is mounted upon or between sheets of glass or other transparent materials.

The individual Polaroid crystals in the film are very small needles whose girth diameter is considerably less than the wave-length of visible light. When light enters one of these crystals, it is divided into two components polarized at right angles to each other; and, by virtue of the dichroism of the crystals, one of these components is absorbed more strongly than the other. The more freely transmitted component is the *desired* component, while the other is the *undesired* component.

We can regard a sheet of Polaroid film as a three-dimensional system of oriented crystals, closely packed together in the matrix. The crystals are so small and their concentration so great that the structure of the film is invisible, except under special conditions. At magnifications of 1100 or greater and with polarized illumination, it is just possible to discern discontinuities in the film.

The light transmitted by Polaroid must involve an aggregate of very nearly coincident light vibration vectors embodying the cumulative action and interaction of the desired components of transmission of successive crystals traversed by the light. At the same time, there is a similar aggregate of light vectors of much smaller magnitude, at right angles to the other, which represents the undesired component in the transmitted light.

The cellulosic matrix is also birefringent. In the manufacture of Polaroid, the mean orientation of the crystals is aligned with one of the two principal directions of vibration of light in the cellulosic sheet. In order to detect the effects of birefringence of the matrix, it is necessary to depart very considerably from normal incidence.

For ordinary practical purposes, the light transmitted by Polaroid may be considered partially plane polarized in the usual sense, as if it were a simple mixture of a plane polarized and unpolarized light. This assumption neglects the slightly imperfect orientation of the crystals, but it is entirely adequate to correlate the simple facts of transmission.

On the assumption that Polaroid is a simple "partial" polarizer, the transmitted light is characterized by a certain relative intensity K and by a certain degree of polarization V. The incident light, of course, is assumed unpolarized. The coefficient K is the ratio of the intensity of the transmitted light (irrespective of its polarization) to that of the unpolarized incident light. The degree of polarization V is the ratio of the intensity of the plane-polarized part to the total intensity of the transmitted light.

The most direct experimental approach to the degree of polarization proceeds by way of the measurement of the ratio of the intensities of the undesired and desired components of the transmitted light. If this ratio is denoted by R, the

[1] Registered trade-name of a material manufactured and sold under (E. H. Land) U. S. Patents 1,918,848; 1,989,371; 1,951,664; 1,956,867; 2,011,553.

[2] Ingersoll, Winans and Krause, J. Opt. Soc. Am. **26**, 233–4 (1936); Strong, J. Opt Soc. Am. **26**, 256 (1936); Tuzi and Nisida, Sci. Pap. Inst. Phys. & Chem. Res. Tokyo **31**, 99–107 (1937).

degree of polarization is

$$V=(1-R)/(1+R).$$

The transmission coefficients for two pieces of Polaroid superposed are easily derived from these quantities. When the polarizing axes are parallel, the transmission is

$$H_1=K^2(1+V^2)$$

and, in like manner, when the axes are crossed, the transmission is

$$H_2=K^2(1-V^2).$$

Instead of the coefficients K and V, one can also use two others that might appropriately be called the *polarized transmission coefficients*, k_x and k_y. The coefficient k_x is here taken to represent the relative intensity of light transmitted by Polaroid when the incident light is plane polarized with its vibrations parallel to those of the undesired component. In like manner, k_y is the measure of the transmission when the vibrations of the plane polarized incident light are parallel to those of the desired component. The following relations are then obvious:

$$R=k_x/k_y,$$
$$V=(k_y-k_x)/(k_y+k_x),$$
$$K=\tfrac{1}{2}(k_y+k_x).$$

Furthermore, the transmission coefficients for superposed pieces of Polaroid, with their axes respectively parallel and crossed are

$$H_1=\tfrac{1}{2}k_y^2(1+R^2)$$

and

$$H_2=k_y^2R.$$

Experimental Procedure

Inasmuch as the usefulness of Polaroid is ordinarily limited to visible light, it is most convenient to use the superior visual methods of photometry in studying its properties. The apparatus used consists essentially of a Bausch and Lomb polarizing photometer whose initial apertures are illuminated from a considerable distance with the image of the ribbon filament of a special General Electric incandescent projection lamp (6 volts, 18 amperes). An image of the biprism in the photometer is focused on the slit of a constant-deviation wave-length spectrometer with an adjustable slit in the focal plane of the eyepiece to isolate narrow regions in the spectrum.

A great deal depends upon the excellence of the analyzing Nicol prism in the photometer. Fortunately, I found several photometer units at my disposal among which there is one whose Nicol is very good. When the field of the photometer is restricted by means of a stop between the biprism and the slit of the spectrometer, this instrument yields excellent extinction in intense light when the axis of the Nicol is crossed with either axis of the Wollaston.

The apertures of the photometer are usually 4 cm apart. This separation is obtained by means of an attached unit containing two small glass rhombs. This unit is removed, exposing the two real apertures within, which are 1 cm apart. This eliminates effects due to changes of phase on internal reflection in the rhombs, and it also makes it possible to work conveniently with small disks of Polaroid to check on variations of its properties across the area of a large parent film.

The specimens are disks, carefully edge ground to a diameter of 1.25 inches. These disks are held by edge friction in a specially designed metal holder in which either one or two disks can be mounted independently and on which their polarizing axes can be oriented to an accuracy of one-tenth of one degree. One must be careful not to strain the glass of the Polaroid disks in order to avoid photoelastic effects.

For the determination of the transmission coefficient, the disk is placed over one and then the other aperture, with its polarizing axis at 45° to the direction of polarization of light admitted by the aperture. This arrangement yields a direct measure of K as defined by the expression $\frac{1}{2}(k_y+k_x)$. The accuracy of this procedure was carefully checked by covering both apertures with a neutral depolarizing material, such as heavy paraffin paper.

In determining the degree of polarization, the Polaroid disk is set to cover both apertures at the same time, its polarizing axis being parallel to the axis of one and then the other aperture. In this arrangement, the photometer reads the ratio R directly.

The basic orientations of the Polaroid disks are established as follows: With the disk covering both apertures, it is turned until the light in

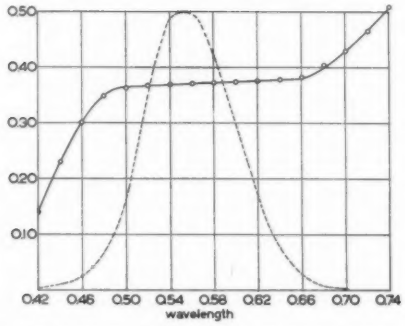


FIG. 1. The spectral distribution of transmission of commercial Polaroid (July 1937). The dotted line is the visibility curve, drawn at half-scale.

either half of the field of view is roughly a minimum. The ratio R is then read for various orientations, at intervals of a degree or less, in the vicinity of this approximate setting. By plotting R with respect to orientation, the position of the minimum of the curve can be found to one-tenth of a degree very quickly. The position of the minimum identifies the orientation of the Polaroid disk when its polarizing axis coincides with the axis of either aperture of the photometer.

Needless to say, all measurements are made with the usual filters in the illuminating system to reduce stray light.

RESULTS

The results given here are averages of many measurements on standard commercial Polaroid manufactured by The Polaroid Corporation during the month of July 1937. The thickness of the film in these pieces of Polaroid is approximately 0.0026 inch.

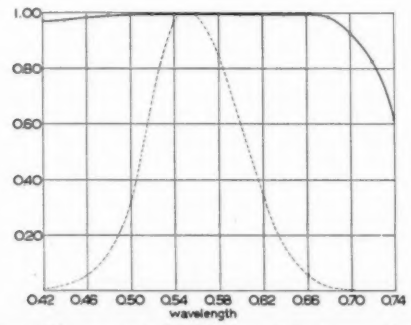


FIG. 2. The spectral distribution of the degree of polarization of light transmitted by commercial Polaroid (July 1937). The dotted line is the visibility curve.

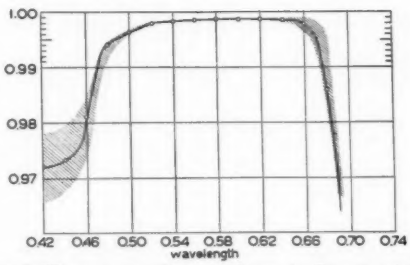


FIG. 3. Upper part of curve shown in Fig. 2, with the vertical scale greatly enlarged. The shaded area shows the range of variation of the degree of polarization of different samples of Polaroid.

Figure 1 shows the spectral distribution of the transmission coefficient, K, from 4200 to 7400A. At the blue end of the spectrum, the curve rises from 0.14 at 4200 to about 0.36 at 5000. It then ascends smoothly and gradually to 0.38 at 6600, beyond which it rises more steeply to 0.51 at 7400. The values of K greater than 0.50 are possible by virtue of the imperfect polarization at the red threshold of the spectrum.

The dotted curve in Fig. 1 is a half-scale representation of the visibility curve of the eye. It is easily seen that the region through which the transmission of Polaroid is nearly uniform coincides with the range within which the sensitivity of the eye is largely concentrated. The effective average transmission of Polaroid is 0.37. This is to be compared with the transmission of the Nicol or Glan-Thompson prisms which, for instance, in the sales literature of Zeiss, has been stated to be 0.40. By using thinner Polaroid film, at a slight sacrifice of polarization, transmissions greater than 0.40 are easily attainable.

An analysis of my transmission measurements points to a relative error of one percent between 5000 and 6000A and of almost two percent at the ends of the spectrum. The differences in transmission of different pieces of Polaroid with the same thickness of film are too small to be measured with certainty.

The degree of polarization of light transmitted by commercial Polaroid is shown in Figs. 2 and 3. In Fig. 2, the complete curve is shown, from 4200 to 7400A. In Fig. 3, the upper part of the curve is drawn to a greatly enlarged scale.

Two small pieces of Polaroid cut from the same run at uniform thickness often exhibit measurable differences in their degree of polariza-

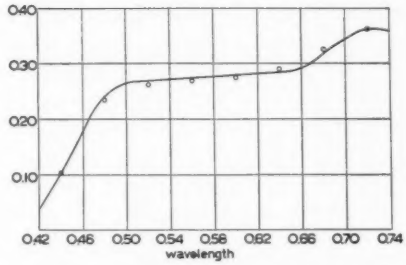


FIG. 4. The calculated transmission of two pieces of Polaroid superposed with their axes parallel. Small circles identify experimentally observed points.

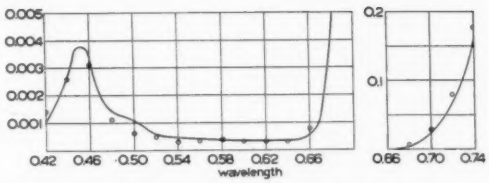


FIG. 5. The calculated transmission of two pieces of Polaroid superposed with their axes crossed. Small circles identify experimentally observed points.

tion. In the middle of the spectrum, these differences are just large enough to be detected, i.e. about 0.0005. At the far ends, however, they are sometimes very marked when studied spectroscopically. The extent of these differences is shown by the shaded area in Fig. 3. They are caused by certain mechanical vagaries of the production machines and they are now being eliminated.

In general, the degree of polarization rises from 0.97 at 4200 to 0.998 or greater at 5400. It then remains practically constant up to a sharp break at 6500 or beyond, as the case may be, and then decreases rapidly.

Measurements of the degree of polarization may be made with surprising accuracy in the middle of the spectrum, where the values of V are nearly unity and the sensitivity of the eye is good. In this region, R is roughly equal to 0.001, and it can be determined to about 12 percent. Since V is equal to $(1-R)/(1+R)$, the error in V is 0.0003. At the blue end of the spectrum, the corresponding error in V is roughly 0.001, and at the red end, beyond 7000A, it is 0.005.

Measurements on pieces of Polaroid made with films of greater than normal thicknesses have shown degrees of polarization as high as 0.9992 in the middle of the spectrum. The average transmission of such pieces is 0.33.

All these data apply to standard Polaroid in which the film is mounted between thin plates of glass. No corrections are made for reflection or collateral absorption losses.

The spectral distributions of transmission through two pieces of Polaroid superposed, with their axes respectively parallel and crossed, are shown in Figs. 4 and 5. The solid lines are calculated from the values of K and V for a single piece: the small circles identify experimentally observed points.

THE USE OF SUPERPOSED PIECES OF POLAROID FOR PHOTOMETRY

Inasmuch as the use of pairs of Nicol prisms and the familiar cosine squared law of relative transmission have long been identified with visual photometry, it is natural to inquire how well the law describes the transmission of light through two pieces of Polaroid superposed, when the angle between their polarizing axes is varied.

It is assumed that Polaroid transmits a desired and an undesired component vibrating at right angles to each other. With reference to Fig. 6, in which part (a) represents the components of polarized transmission of the first piece of Polaroid and part (b) those of the second, it follows that the total intensity of light transmitted by the two pieces is

$$J=\tfrac{1}{2}I_0(k_y(k_y\cos^2\theta+k_x\sin^2\theta)+k_x(k_y\sin^2\theta+k_x\cos^2\theta)),$$

which immediately reduces to

$$J=\tfrac{1}{2}I_0k_y^2((1+R^2)\cos^2\theta+2R,\sin^2\theta).$$

This expression must now be compared with

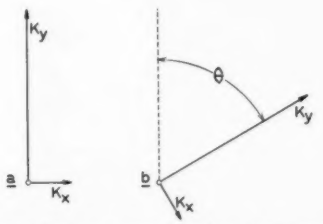


FIG. 6. Vector diagram accompanying the discussion of the photometrical use of Polaroid.

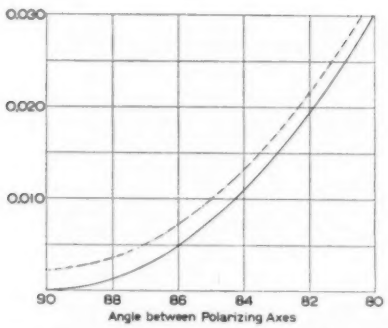


FIG. 7. The dashed curve shows the effective relative transmission (for visual purposes) of two pieces of Polaroid superposed as a function of the angle between their polarizing axes. The solid line represents the ideal condition.

the ideal relation

$$J' = \tfrac{1}{2} I_0 k_y^2 \cos^2 \theta.$$

The angle θ is the angle between the two polarizing axes, and I_0 is the intensity of the unpolarized incident light.

The difference between the expressions for J and J' arises from the quantity R. Inasmuch as R is a function of the wave-length, the same is true of the disparity between J and J'.

This immediately raises the question of the conditions under which the photometrical application is to be made; and these conditions involve the spectral distributions of intensity of the source and of sensitivity of the receiver.

The case of primary interest is that of visual photometry, with an incandescent source of light. Calculations for this case have been carried through, using the familiar data for the visibility curve of the eye and of the distribution of intensity of light from a tungsten filament. At each wave-length (at intervals of 200A) the value of J is weighted by the product of the corresponding ordinates of the intensity and visibility curves. The sum of these weighted values of J is then divided by the sum of the weights, yielding a value for an effective transmission coefficient for visual purposes.

Some of the results of this calculation are shown in Fig. 7 in which the dashed curve shows the *relative* value of the effective visual transmission as defined above, plotted with respect to θ, the angle between the polarizing axes of the two pieces of Polaroid. The solid curve is a plot of $\cos^2 \theta$, representing the ideal condition. In the range of Fig. 7, the vertical separation of the two curves is almost uniformly equal to 0.002. This separation decreases to 0.001 at about 45°, and it vanishes when both curves reach unity at $\theta = 0$.

The spectral variation of the ratio R gives rise to a variation with respect to θ of the spectral distribution of intensity of the transmitted light. However, this change in the chromaticity of the light is negligible, except for values of θ near extinction, where the departure from the ideal relationship becomes relatively very large.

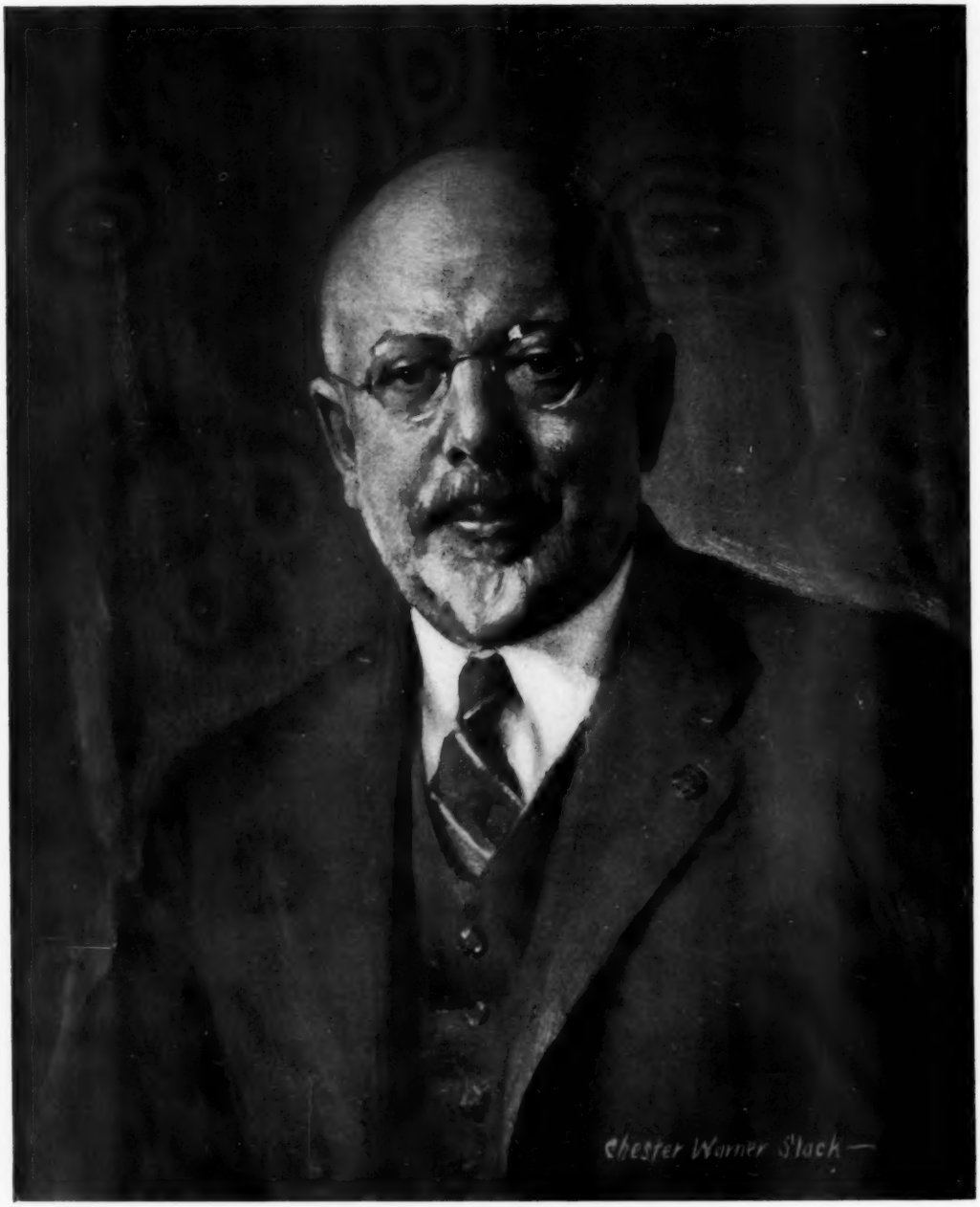
It is often desirable to use superposed pieces of Polarioid to control the relative intensity of light admitted to a photo-cell. Since these cells are often very sensitive to red and infrared light, it is necessary to restrict the light in one way or another to such wave-lengths for which the polarization of Polaroid is effective.

In conclusion, I would express my thanks to Professor Theodore Lyman, the Director of the Jefferson Physical Laboratory at Harvard, for giving me the use of the facilities of his optical laboratory.

The Frederic Ives Medal for 1937

Awarded by The Optical Society of America to Herbert E. Ives,
Charter Member and Past-President of the Society,
and Director of Electro-optical Research in the Bell Telephone Laboratories,
for distinguished work in optics.

This medal, awarded biennially, was endowed in 1928 in honor of Frederic Ives, distinguished for his pioneer contributions to color photography, photoengraving, three-color process printing, and other branches of applied optics.



DR. HERBERT EUGENE IVES

(From a Trichromatic Painting by Chester Warner Slack.)

Doctor Herbert Eugene Ives

IVES MEDALIST FOR 1937

AT its Lake Placid meeting in October, 1937, the Optical Society of America awarded the Frederic Ives Medal to Dr. Herbert E. Ives, Director of Electro-optical Research in the Bell Telephone Laboratories. This medal is awarded biennially for distinguished work in optics, and its past recipients have been as follows:

In 1929, Edward Leamington Nichols;
In 1931, Theodore Lyman;
In 1933, Robert Williams Wood;
In 1935, George Ellery Hale.

The presentation of the medal to Dr. Ives took place at the Annual Dinner of the Society, which was held in the Lake Placid Club, with nearly one hundred members and guests of the society attending.

After having stated the conditions of the award of the medal, President Hardy reviewed the contributions to optics of Frederic Ives, stressing the type of scientific achievement which it was the purpose of the medal to commemorate and to stimulate. The report to the Board of Directors of the Society of the Committee on Award of the Frederic Ives Medal was then reviewed by the chairman of that Committee, after which President Hardy made the formal presentation of the medal. Dr. Ives responded fittingly, reviewing highlights of his scientific career, and presenting interesting historical material illustrating some of the apparatus developed and used by his father, Frederic Ives, in whose honor the medal was founded.

In reviewing the report of the Committee on Award, its chairman emphasized the diversity of the contributions of Dr. Ives to optics, and especially to applied optics. In the period from 1906 to 1937 Dr. Ives published more than one hundred papers in such fields as the photoelectric effect and its applications, spectrophotometry, the efficiency of illuminants, television and picture transmission over wires, the theory of vision, standards of illumination, stereoscopy, color photography and theory of color, photoengraving, phosphorescence, and many others. A partial but representative list of these papers is appended.

Herbert E. Ives received the B.S. degree from the University of Pennsylvania in 1905. He was a fellow at Johns Hopkins University from 1906 to 1908, at which time he received his Ph.D. degree. Yale, Dartmouth, and Pennsylvania have since awarded him honorary Sc.D. degrees. He served, first as assistant and later as assistant physicist, at the National Bureau of Standards during 1908 and 1909, after which he went as physicist to the National Electric Lamp Association in Cleveland. In 1912 he went to the United Gas Improvement Co. In 1918 he transferred to the Western Electric Co., and since their inception in 1925 he has been with the Bell Telephone Laboratories.

Dr. Ives was successively Captain and Major in the United States Army during 1918, being in charge of aerial photographic research. Many of his most important contributions have been to this field, especially to stereoscopic photography.

While Dr. Ives did not invent the method of flicker photometry, his early papers explaining why results previously obtained by this method showed discrepancies have become classics in the optical literature. The importance of his early papers on color and on the efficiencies of illuminants is attested to by the frequency with which they are mentioned in papers published by other workers in the field.

The first work of Dr. Ives in the telephone laboratories was on electrical contacts, this being followed by investigations of photoelectric cells and of their possible uses in the communication industry. He was in charge of the general development of picture transmission, first demonstrated in 1924, and of the television demonstrated in 1927. Dr. Ives later engaged in the development of outdoor television and of color television as demonstrated in 1929. Two-way television was demonstrated for the first time in April, 1930. In recent years he has made important contributions to the projection of

motion pictures in relief, to the theory of the artist's palette, and to an understanding of photoelectric emission.

The appended list of the scientific contributions of Dr. Ives gives a good idea of the catholicity of his interest in optics, but the importance and distinction of his contributions can best be judged by the esteem in which he is held by fellow-workers in his chosen field.

GEORGE R. HARRISON
Chairman, Committee on Award of the Frederic Ives Medal

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